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Absorption Spectra and Band Structure of Mixed Frenkel-Charge-Transfer Vibronic States in One-Dimensional Molecular Crystals

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We discuss the excited state structure of a one-dimensional molecular crystal. As in the Holstein model, we consider one Frenkel exciton with nearest-neighbor hopping and linear coupling to one internal vibration. Additionally, we include charge-transfer (CT) excitons that couple to the same vibrational mode and mix with the Frenkel exciton. The excited states of this model Hamiltonian are investigated by numerical diagonalization. For this, we represent the Hamiltonian in a displaced oscillator (Lang-Firsov) basis and use a problem-adapted truncation scheme for the phonon basis. Thus, the complete optical spectrum becomes accessible for weak up to intermediate electronic coupling. As an example, we discuss the exciton structure of the quasi-one-dimensional molecular crystals of PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) and MePTCDI (N-N′-dimethylperylene-3,4,9,10-dicarboximide). The experimental linear absorption spectra can be well described by the $k = 0$ states using appropriate parameter sets. We present the resulting band structure and compare the $k = \pi$ states with emission spectra.

I. INTRODUCTION

There is revived interest in organic semiconductors based on π-conjugated molecules because of their potential applications in organic LEDs, solar cells and low-cost electronic circuits. For all opto-electronic applications, a detailed understanding of the photo-excited states becomes desirable. Therefore, we investigate the excited states for a Holstein model system of a one-dimensional molecular chain with Frenkel excitons, charge-transfer (CT) excitons, and linear coupling to one internal vibration. Such a model is approximately realized by some quasi-one-dimensional molecular crystals, in particular by PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride), MePTCDI (N-N′-dimethylperylene-3,4,9,10-dicarboximide) or related perylene derivatives.

All recent interpretations of PTCDA crystal absorption spectra [1–5] use the framework of small-radius excitons. However, there is no general agreement yet about the role of CT excitons, about the choice between a complete Holstein model or a molecular vibron model, and about actual values of various interaction parameters.

In our recent work [5], we presented a numerical scheme for the calculation of the complete optical spectrum in a Frenkel-CT Holstein model. We discussed the applicability of the molecular vibron model, in which only joint exciton-phonon configurations are considered. The molecular vibron model was compared to numerical solutions of the complete Holstein problem with separated exciton-phonon configurations. We described experimental absorptions spectra of PTCDA and MePTCDI as the $k = 0$ states of such a model and suggested suitable parameters. Here, we repeat some key results and extend the discussion to the $k = \pi$ states and emission spectra.

II. MODEL HAMILTONIAN AND NUMERICAL DIAGONALIZATION

For the Frenkel excitons, we use a one dimensional Holstein model with a nearest-neighbor Frenkel-exciton transfer-integral J and a linear exciton-phonon coupling constant g. The Holstein Hamiltonian for Frenkel excitons can be very naturally extended to include charge-transfer (CT) states (cf. Ref. [5]). We consider nearest-neighbor CT states in which an electron is transferred from lattice site n to site $n+f$ ($f = \pm 1$) without changing the spin. The on-site energy of a CT state in the molecular limit is denoted by D (relative to the Frenkel exciton on-site energy at zero in our energy units). The electron or hole excitation of the CT states are assumed to couple to the same effective vibrational coordinate as the Frenkel exciton with an electron-phonon coupling constant g_e and a hole-phonon coupling constant g_h. The mixing between Frenkel and CT excitons can be described by the charge-transfer integrals $t_\mathrm{e}/t_\mathrm{h}$, which stand for the transfer of an individual electron/hole between the site of a Frenkel exciton and its nearest neighbor (cf. [1, 2]).

For weak up to intermediate electronic coupling ($J < g\hbar\omega$), this Hamiltonian can be investigated by numerical diagonalization. We use the solutions of the molecular limit ($J = t_\mathrm{e} = t_\mathrm{h} = 0$) as basis states $|n\, f\, \underline{\nu}\rangle$ (cf. Ref. [5]). These states have localized Frenkel ($f = 0$) or CT ($f = \pm 1$) excitons at position n and any combination $\underline{\nu} = |\ldots \nu_{-1}\tilde{\nu}_0\nu_1 \ldots\rangle$ of vibrational excitations at arbitrary lattice sites. The ν_m are the phonon occupation numbers at the site $n + m$ (relative to the exciton). The key point is that in the solutions of the molecular limit the vibrational potentials are displaced at the sites that are occupied by an exciton or a charge carrier and then also the occupation numbers ν_m refer to the correspondingly displaced potential. For a Frenkel exciton basis state ($f = 0$), the displaced center position is denoted by the tilde. Fourier transformation of the real-space states $|n\,f\,\underline{\nu}\rangle$ gives basis states $|k\,f\,\underline{\nu}\rangle$ in momentum-space, where k is now a good quantum number. For given k, the matrix elements between the basis states can be calculated and the eigenstates can be obtained by numerical diagonalization.

For direct diagonalization, the number of basis states has to be finite. A complete phonon-cloud basis for a chain of N molecules consists of N-boson states and leads to huge basis sets even for small occupation numbers. But a far smaller basis is sufficient to calculate the absorption spectrum. Among the Frenkel exciton basis states $|k\,0\,\underline{\nu}\rangle$, optical absorption from the electronic and vibrational ground state only reaches joint exciton-phonon configurations of the form $|\underline{\nu}\rangle = |\ldots 000\tilde{\nu}_0 000\ldots\rangle$. Separated configurations with localized phonon excitations at sites different from the exciton (any $\nu_m \neq 0$ for $m \neq 0$) cannot be reached optically. For $J = 0$, these separated configurations cannot mix with the optically active basis states either. Then, instead of the N-particle states $|\underline{\nu}\rangle$ we can use the one-particle states $|\nu_0\rangle$ (molecular vibron model).

For $|J| > 0$, the separated configurations can mix with the joint configurations. That means, the optically excited eigenstate involves basis states in which localized phonons are excited at arbitrary distance from the site of the localized exciton. However, the contribution of such separated configurations decreases with increasing exciton-phonon separation. Thus, the exciton will be surrounded by a *localized* phonon cloud. The localized nature of phonon clouds is the motivation for our choice of basis functions. Instead of N-dimensional cloud states $|\underline{\nu}\rangle$, a finite range $|\nu_{-M}\ldots\tilde{\nu}_0\ldots\nu_M\rangle$, with M denoting the extension of the phonon cloud, will be sufficient. In Ref. [5] we demonstrated, how the limit for M and for additional restrictions of maximum occupation numbers can be increased until convergence is reached.

From the eigenstates $\Psi_j(k)$, the transition dipole moments $\vec{P}_j$ can be reduced to the transition moments of the basis states, which gives a Frenkel contribution $P_{\mathrm{FE}\,j}(k)$ and a symmetric CT contribution $P_{\mathrm{CT}\,j}(k)$ (cf. Ref. [5]). In first approximation, the CT transition dipole will be small and $\vec{P}_j$ will mainly be given by its Frenkel component. The k-dependent spectral weights $P^2_{\mathrm{FE}\,j}(k)$ and $P^2_{\mathrm{CT}\,j}(k)$ represent the electronic character (Frenkel or symmetric CT) of state j (cf. Ref. [5]).

III. EXPERIMENTAL SPECTRA AND EXCITON BAND STRUCTURE

Section II provides the scheme with which energies E_j and transition dipoles $\vec{P}_j$ of the eigenstates of the one-dimensional Holstein problem can be obtained for given parameters. In Ref. [5], we suggest parameter sets that can describe absorption spectra of PTCDA and MePTCDI as $k = 0$ states of the Frenkel-CT-Holstein Hamiltonian. From monomer absorption spectra we took $\hbar\omega = 0.17\,\mathrm{eV}$ and $g = 0.88$. We neglected a possible contribution of $\vec{p}_{\mathrm{CT}}$ to the absorption spectrum and we assumed for simplicity $g_{\mathrm{e}} = g_{\mathrm{h}} = g/\sqrt{2}$ and $t_{\mathrm{e}} = t_{\mathrm{h}} = t$. The key-parameters obtained from the fit are for PTCDA $J = 42\,\mathrm{meV}$, $D = 97\,\mathrm{meV}$, $t = 85\,\mathrm{meV}$ and for MePTCDI $J = 46\,\mathrm{meV}$, $D = 240\,\mathrm{meV}$, $t = 115\,\mathrm{meV}$. Both parameter sets correspond to a strong mixing of Frenkel and CT excitons.

The structure of the eigenstate spectrum at $k = 0$ is best visualized by the Frenkel ($P^2_{\mathrm{FE}\,j}$) and CT ($P^2_{\mathrm{CT}\,j}$) characters of the states. We illustrate these characters in Figs. 1(b) and 2(b). The electronic Frenkel character determines the absorption coefficient α. The comparison of the experimental absorption coefficient and the model fit is given in the panels (a). Note that α is not simply proportional to $P^2_{\mathrm{FE}\,j}$, since it also depends on the refractive index (cf. Ref. [5]). We emphasize that for PTCDA similarly good fits of the experimental spectra can be obtained for different parameter sets with varying degree of CT mixing. Even total neglect of CT states would give a satisfactory fit with a Frenkel transfer integral of $70\,\mathrm{meV}$. Such a value corresponds to the three-dimensional Frenkel exciton model for PTCDA in Ref. [4]. We present the scenario of strong Frenkel-CT mixing because it corresponds to the situation in the similar compound MePTCDI and to previous interpretations [1–3]. Electroabsorption spectra rather than linear absorption make it necessary to invoke CT participation [1, 3].

We now discuss what the proposed model for the absorbing states ($k = 0$) means for the total band structure. The resulting states at $k = \pi$ are shown in Figs. 1(d) (PTCDA) and 2(d) (MePTCDI). In order to rationalize the k dependencies, we also show the purely electronic bands for the complete k-range in the panels (c). The electronic bands represent the situation, in which all vibrational parts are neglected in the Hamiltonian. Then, we only have a mixture of electronic Frenkel and CT excitons. An unmixed anti-symmetric CT combination can be separated from the problem [2], and we get two mixed Frenkel-CT exciton bands. The k-dependent character of the bands is shown by the shaded stripes. These electronic bands visualize how the electronic Frenkel character disperses to lower energies as a result of the positive Frenkel exciton hopping integral J. The center of mass of the CT character remains at a constant position since a CT dispersion is not considered in the model. Furthermore, for this special choice of charge-transfer integrals $t_{\mathrm{e}} = t_{\mathrm{h}}$, the Frenkel and CT states do not mix at $k = \pi$ (cf. Ref. [1, 2]). As at $k = 0$, the inclusion of exciton-phonon coupling at $k = \pi$ transforms the two electronic states into a broad vibronic spectrum. With the model parameters from the absorption fit, the lowest $k = \pi$ state lies at $E = 2.18\,\mathrm{eV}$ for PTCDA and at $E = 2.06\,\mathrm{eV}$ for MePTCDI.

The band bottom of the exciton band structure is a starting point for the discussion of emission spectra since all photoexcited states will rapidly relax to these lowest states. The transition from these $k = \pi$ states to the total ground state is strictly dipole-forbidden, at least in perfect crystals. However, transitions to $k = \pi$ phonons in the electronic ground state are allowed. We indicate the resulting transition energies (including the forbidden 00-transition) in the panels (e). For a qualitative comparison, these transition energies are compared to transient low-temperature photoluminescence spectra of single crystals in the panels (f) of both figures. The comparison

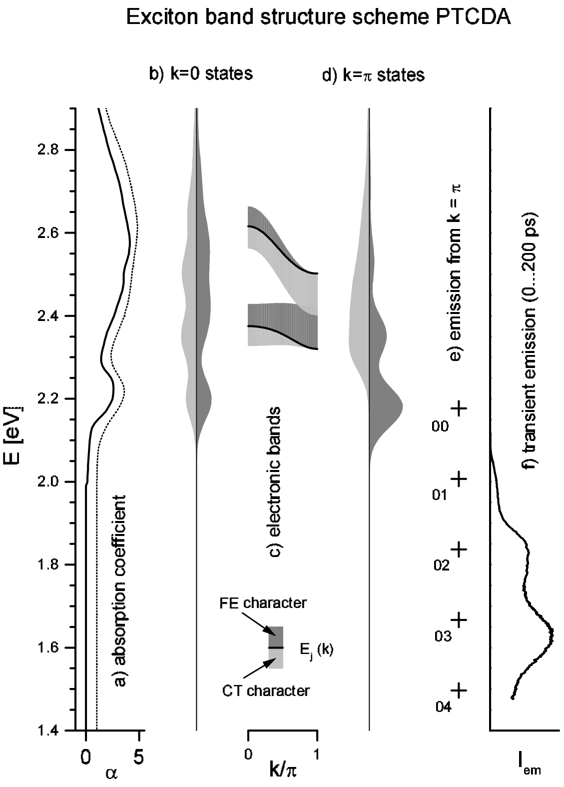

FIG. 1: Suggested exciton band structure in PTCDA and experimental spectra. a) solid line: low temperature absorption spectrum of thin poly-crystalline film as reported in Ref. [5], absorption coefficient α in $10^5\,\mathrm{cm}^{-1}$; dotted line: absorption coefficient from model fit (plotted with offset $+1\times10^5\,\mathrm{cm}^{-1}$). b) Vibronic model states at $k=0$. The right side (dark shading) gives the Frenkel character $P^2_{\mathrm{FE}\,j}$ of the states j, the left side the CT character $P^2_{\mathrm{CT}\,j}$. Instead of the closely lying individual states, we show a broadened spectrum that summarized the net contribution. The Frenkel character at $k=0$ determines the oscillator strength and corresponds to the model absorption spectrum in (a). c) Electronic bands $E_j(k)$. These bands show the overall dispersion and the k-dependent Frenkel-CT mixing, which result from the electronic interaction parameters. d) Vibronic model states for $k=\pi$. e) Emission energies for transitions from the lowest $k=\pi$ state to the vibrational levels of the electronic ground state. The highest transition (00) is strictly dipole-forbidden. f) transient emission spectrum of a PTCDA single crystal at $10\,\mathrm{K}$ (time window $0\ldots200\,\mathrm{ps}$), corrected for spectral response of the set-up.

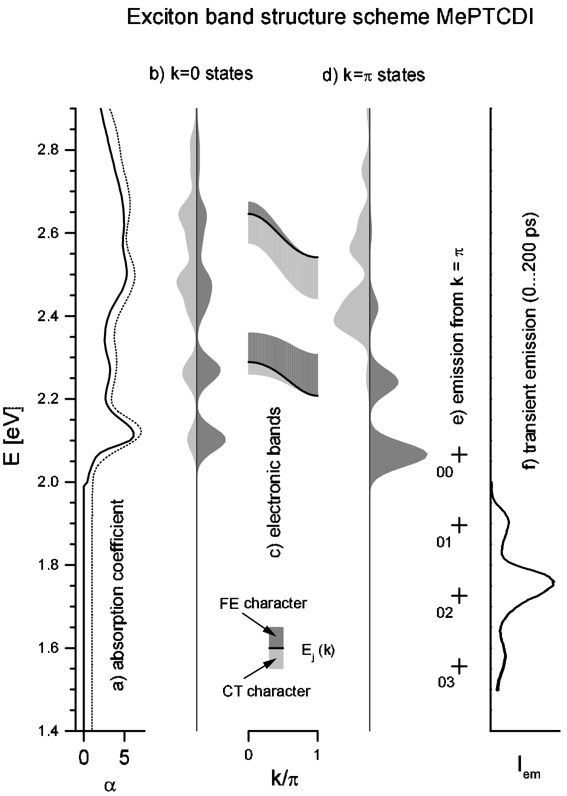

FIG. 2: Suggested exciton band structure in MePTCDI and experimental spectra. For detailed explanations see Fig. 1. The experimental absorption spectrum in (a) is measured at $10\,\mathrm{K}$ at a highly oriented poly-crystalline film with polarization parallel to the strong Davydov component (crystallographic b-axis), cf. Ref. [2]. The transient emission spectrum in (f) is measured at $4\,\mathrm{K}$ at a single crystal, time window $0\ldots200\,\mathrm{ps}$, corrected for spectral response of the set-up, from Ref. [7].

shows that the energetic positions of the 01 and 02 transition do approximately agree with the peaks in the emission spectra. This supports the order of magnitude of the model parameters, especially the relatively small value of the Frenkel hopping J. A larger J, as could be expected from quantum chemical arguments [1], would give a larger separation between the lowest absorption peak and the 01-emission peak.

The assignment of the emission spectra is still very tentative, since the spectra do not show an exact vibronic progression and the decay times of the peaks are slightly different, which becomes much more pronounced at higher temperatures. Furthermore, the emission spectra sensitively depend on the concrete sample configurations, on the considered time scale (up to cw) and on the temperature. This leads to widely varying emission spectra and assignments. It is not clear at this stage, to what extend extrinsic defects or further intrinsic effects determine the emission behavior. In particular, a strong coupling to external phonon modes, corresponding to excimer emission, can be expected as an additional effect (cf. e.g. [6]). All these effects might be reasons for the discrepancies, which are particulary pronounced in the lowest PTCDA emission peak.

In spite of these potential complications, the band structure within a Holstein model is the starting point for a discussion of emission spectra and relaxation processes after photo-excitation. In this work, we showed how the excited states can be modelled in the framework of a Holstein Hamiltonian with inclusion of CT states. Our numerical approach gives the possibility to investigate the exciton-phonon coupling with correct inclusion of separated exciton-phonon configurations. On this basis, the important approximation of the molecular vibron model (only joint exciton-phonon configurations) can be tested and then used for further extensions of the model.

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[1] M. H. Hennessy, Z. G. Soos, R. A. Pascal Jr., and A. Girlando, *Chem. Phys.* **245** (1999) 199.
[2] M. Hoffmann, K. Schmidt, T. Fritz, T. Hasche, V. M. Agranovich, and K. Leo, *Chem. Phys.* **258** (2000) 73.
[3] G. Mazur, Ph. D. thesis, Jagiellonian University Cracow, 2001.
[4] I. Vragovic, R. Scholz, and M. Schreiber, *Europhys. Lett.* **57** (2002) 288.
[5] M. Hoffmann and Z. G. Soos, *Phys. Rev. B* **66** (2002) 024305.
[6] T.-W. Wu, D. W. Brown, and K. Lindenberg, *Phys. Rev. B.* **47** (1993) 10122.
[7] T. Canzler, Ph.D. thesis, TU Dresden, 2002.